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3,396,026

PHOTOGRAPHIC CAPSULAR PRODUCTS

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No Drawing. Filed Mar. 25, 1963, Ser. No. 267,847
9 Claims. (Cl. 96—94)

ABSTRACT OF THE DISCLOSURE

This invention relates to microscopic capsules having walls which include a substantially continuous polymeric layer comprising a coacervate containing a low isoelectric point gelatin and a gelatin derivative, which derivative comprises the reaction product of gelatin and a derivatizing agent which reacts with at least a portion of the gelatin's amino groups, surrounding a nucleus comprising a water-immiscible medium and which are adapted to retain materials suitable for use in photographic black and white and color processes.

The copending application of William J. McCune, Jr., filed May 9, 1961, Ser. No. 108,774, now Patent 3,276,869, discloses the use of minute capsules for use in photographic processes. In one embodiment, the minute capsules contain dye developers for use in preparing color images by the diffusion transfer process. In another embodiment, the microscopic capsules are coated with a layer of silver halide. U.S. Patent No. 2,983,606, issued May 9, 1961, to Howard G. Rogers, discloses processes employing dye developers to form color transfer images and products useful therein. The copending application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135, filed Feb. 13, 1956, discloses the use of such dye developers in integral multilayer negatives to give multicolor transfer images.

Accordingly, it is one object of this invention to provide novel minute capsules for use in the photographic products and processes.

Another object of this invention is to provide minute capsules whose walls comprise photographic gelatin.

Still another object of this invention is to provide capsules whose walls comprise gelatin and photosensitive silver halide.

Still another object of this invention is to provide novel processes for the preparation of minute capsules.

Still another object of this invention is to provide capsules of the aforementioned structure wherein color-providing materials are encapsulated.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

Methods of preparation of microscopic, pressure-rupturable capsules containing a water-immiscible medium are well known to the art. Generally, such capsules are formed by deposition of a complex colloid material around microscopic droplets of a water-immiscible medium by the process of causing coacervation, by dilution or adjustment of the pH, to occur in a mixture of two different colloid salts in which the water-immiscible material is dispersed as droplets, and then gelling the complex

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colloid. Generally, a complex colloid material is formed of an aqueous solution of one colloid, emulsifying the nuclei material or internal phase therein and mixing the thus-formed emulsion with an aqueous salt of another colloid. Alternatively the two colloid materials may be made and mixed and the water-immiscible material emulsified therein. Coacervation is then brought about by dilution and/or by adjusting the pH of the mixture. The gellable colloid materials used in the solutions must be ionizable and the art has taught that the sols must exist in the mixture with opposite electric charges. One well-known system comprises high isoelectric point gelatin as the positive colloid, gum arabic as the negative colloid, and water. A solution of these materials is prepared and the pH and concentration of the system is adjusted to a point where coacervation occurs. A water-immiscible material may then be added to the solution and the gelatin-gum arabic coacervate phase will deposit around the water-immiscible droplets thereby encapsulating the water-immiscible medium.

In photographic products and processes, low isoelectric point gelatin is preferred as a colloid binder over higher isoelectric point gelatin. Accordingly, it becomes considerably more desirable to prepare minute capsules which are to be used in photographic products and processes with low isoelectric point gelatin. Also, gum arabic is not available domestically and problems of supply may arise. Therefore, the problem that presents itself is to replace a positive colloid with a negative colloid and still provide a system in which a coacervate can be formed.

The novel process of this invention comprises encapsulation of water-immiscible materials in low isoelectric point gelatin, particularly photographic grade gelatin, to form minute capsules.

In one embodiment of the present invention, the encapsulating wall material comprises low isoelectric point gelatin and, as a second colloid material, a gelatin derivative comprising the reaction product of a dicarboxylic acid anhydride and gelatin.

In carrying out the novel process of this invention, a solution of low isoelectric point gelatin is prepared and a solution of a second colloid is added. With constant stirring throughout, the temperature and pH of the system is adjusted to provide a coacervate phase of the gelatin and the second colloid. The water-immiscible internal phase material is then added to the coacervate and the solution is cooled slowly. Capsules are formed by the deposition of the complex colloid comprising gelatin and the second colloid around the droplets of the internal phase. The capsular walls are also hardened by the lowering of the temperature. The thus-formed capsules may then be hardened by appropriate means, for example, rapid cooling and/or the addition of the hardening agent such as glutaraldehyde. The hardened capsules may then be isolated and dried and utilized in the desired appropriate manner.

As examples of suitable dicarboxylic acid anhydrides which may be reacted with gelatin to form gelatin derivative reaction products, mention may be made of phthalic anhydride, tri-mellitic anhydride, succinic anhydride and glutaric anhydride. The type of gelatin which is reacted with the dicarboxylic acid anhydride is not critical; high or low isoelectric point gelatin may be used. It should be noted, however, that certain anhydrides are known which will cross-link gelatin. Therefore, these materials should be avoided when selecting anhydrides to prepare a gelatin product for use as the second colloid in this invention. Gelatin-anhydride reaction products are prepared according to the procedure set forth in U.S. Patent No. 2,525,753.

It should be understood that the dicarboxylic acid anhydrides suitable for use in this invention may have other

carboxylic acid groups as well as the two that make up the anhydride groups.

It should be understood that while gelatin derivatized with dicarboxylic acid anhydrides is one of the preferred materials for use as the second colloid gelatin derivatized with other materials which will react with the amino groups of the gelatin is also useful provided that carboxylic acid groups are also added to the gelatin. For example, gelatin derivatized with p-carboxybenzenesulfonyl chloride may also be suitable for use in this invention as the second colloid.

It has also been found that minute capsules containing photosensitive silver halide salts in the capsule walls can be prepared by the novel process of this invention. The aforementioned capsules comprise gelatin with silver halide deposited therein encapsulating an internal phase material. Gelatin-silver halide capsules may be prepared by forming a coacervate of a solution of gelatin-silver halide emulsion and a second colloid, such as the reaction product of gelatin and a dicarboxylic acid anhydride in accordance with the above-disclosed procedure.

The gelatin-silver halide emulsion is prepared by procedures well known to the art, for example, by reacting a water-soluble silver salt, preferably silver nitrate, with at least one water-soluble halide salt, preferably sodium or potassium bromide, most preferably in combination with sodium or potassium iodide, in an aqueous solution of a low isoelectric point gelatin colloid peptizing agent. Additional preparation and sensitization may be carried out by any of the accepted procedures known to the art.

The terms "sensitive," "photosensitive" and "sensitized" and other terms of similar import are herein employed in the generic sense to describe materials possessing physical and chemical properties which enable them to form usable images when exposed to actinic radiation.

By means of the above-described novel process of this invention, solids as well as solutions and suspensions may comprise the internal phase. Solid materials may then be encapsulated by three methods: (1) by direct encapsulation of a solid, (2) by the encapsulation of a solution of the solid in a volatile solvent, and evaporating the solvent after the formation of the capsule, thereby leaving the solid inside, and (3) by the encapsulation of the solid suspended in a material, preferably an organic solvent which is also immiscible in the aqueous coacervate system.

The following nonlimiting examples illustrate the preparation of capsules within the scope of this invention.

Example 1

The pH of 173 ml. of 8% aqueous solution of the reaction product of gelatin and phthalic anhydride (prepared according to the method disclosed in U.S. Patent No. 2,525,753) was adjusted to a pH of 6.5 and added to 700 ml. of water at 45° C. 200 ml. of a 10% aqueous solution of low isoelectric point gelatin was adjusted to a pH of 6.5 and added to the gelatin derivative solution. The pH of the combined solution was then adjusted to 4.5 with acetic acid. 190 ml. of toluene was then added to the solution with vigorous agitation and the mixture was then allowed to cool gradually to about 25° C. The temperature of the solution was then dropped rapidly to 10° C. with a Dry Ice acetone bath. 10 ml. of glutaraldehyde was then added to the solution and the capsules were isolated and dried.

It should be noted that the gelatin-silver halide mixture must be in the form of an emulsion prior to the addition of the second colloid in order to insure that the silver halide will be present in the walls of the capsules. For example, if silver halide were added to a solution of gelatin and capsule preparation carried out, the silver halide itself would be encapsulated as the internal phase but would not be present to any extent in the capsule wall. It should be noted further that the present invention provides silver halide to the capsule walls in the same operation that prepares the capsules themselves and that the

silver halide is a component part of the wall, whereas the above-mentioned copending application, Serial No. 108,774, discloses a separate layer of silver halide deposited on the wall of the capsule after the capsule has been prepared.

The copending application of Lloyd D. Taylor, Ser. No. 267,838, filed Mar. 25, 1963, discloses and claims minute capsules whose walls comprise a single colloid material. It should be understood that a photosensitive silver halide emulsion can be prepared utilizing said single colloid and the thus-prepared colloid can be used in the preparation of capsules which contain silver halide in the capsular walls according to the procedure of the above-noted copending application Ser. No. 267,838, filed Mar. 25, 1963.

In preparing capsules by the novel process of this invention, the agitation or stirring action given the colloid system is determinative of the size of the droplets of water-immiscible phase and ultimately the size of the capsules. The more vigorous the stirring action, the smaller the size of the droplet. For example, capsules about 1 to 10 microns in size may be prepared using the stirring action of a Waring Blendor. Larger size capsules would be prepared by less vigorous stirring action. Capsules prepared by the novel process of this invention are in the 1 to 100 micron range.

The complex colloid system in this invention utilizes what is essentially two negative colloids at an acid pH. The difference in charge between the colloids is one of degree, not kind.

The novel capsules prepared by the process of this invention which contain color-providing substances or which comprise walls of gelatin containing photosensitive silver halide are useful in photographic products and processes. For example, such capsules may be used in photosensitive elements disclosed in the above-mentioned copending application, Ser. No. 108,774. It should be understood that, in photographic applications, the internal phase may be extracted from the capsules by an aqueous alkaline solution. Capsules within the scope of the present invention may also be used in printing or reproductions processes. For example, a dye or printing oil may be incorporated into the internal phase prior to coacervation and a layer of the capsules printed on a sheet of paper. By the application of pressure in a particular pattern, the capsules will rupture liberating the dye or oil thus reproducing the original pressure pattern on the paper.

Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A process of making microscopic capsules which comprises, in combination, the steps of:

(1) providing a fluid mixture which comprises an aqueous solution of a low isoelectric point gelatin and a gelatin derivative, said gelatin derivative comprising the reaction product of gelatin and a gelatin derivatizing agent which reacts with at least a portion of the amino groups of gelatin to provide neutralization of at least a portion of the positive charges provided to the gelatin molecule, in aqueous solution, by said amino groups, at least one of said gelatin and said gelatin derivative having associated therewith a dispersion of photosensitive silver halide, and a water-immiscible medium, whereby droplets of said water-immiscible medium are provided dispersed in said aqueous solution;

(2) adjusting the pH and temperature of the fluid mixture to cause coacervation of said gelatin and said derivatized gelatin, whereby said coacervate deposits around the individual droplets of said water-immiscible medium, individually encapsulating said droplets;

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- (3) gelling said coacervate by cooling said capsules below the gelling temperature of said coacervate.
2. The process as defined in claim 1 wherein said gelatin derivatizing agent comprises a dicarboxylic acid anhydride.
3. A process as defined in claim 1 wherein said water-immiscible medium comprises a dye developer.
4. A process of making microscopic capsules which comprises, in combination, the steps of:
- (1) providing a fluid mixture which comprises an aqueous solution of a low isoelectric point gelatin and a gelatin derivative, said gelatin derivative comprising the reaction product of gelatin and a gelatin derivatizing agent which reacts with at least a portion of the amino groups of said gelatin to provide neutralization of at least a portion of the positive charges provided to the gelatin molecule, in aqueous solution, by said amino groups, and a water-immiscible medium comprising a dye developer, whereby droplets of said water-immiscible medium are provided dispersed in said aqueous solution;
- (2) adjusting the pH and temperature of the fluid mixture to cause coacervation of said gelatin and said derivatized gelatin, whereby said coacervate deposits around the individual droplets of said water-immiscible medium, individually encapsulating said droplets;
- (3) gelling said coacervate by cooling the capsules below the gelling temperature of said coacervate.
5. Microscopic capsules comprising a substantially continuous polymeric layer surrounding a nucleus comprising a water-immiscible medium, said polymeric layer comprising a coacervate containing a low isoelectric point gelatin and a gelatin derivative which comprises the reaction product of gelatin and a gelatin derivatizing agent which reacts with at least a portion of the amino groups of gelatin to provide neutralization of at least a portion of the positive charges provided to the gelatin molecule,

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in aqueous solution, by said amino groups, at least one of said gelatin and said gelatin derivative having associated therewith a dispersion of photosensitive silver halide.

6. A product as defined in claim 5 wherein said gelatin derivatizing agent comprises a dicarboxylic acid anhydride.

7. A product as defined in claim 5 wherein said water-immiscible medium comprises a dye developer.

8. Microscopic capsules comprising a substantially continuous polymeric layer surrounding a nucleus comprising a water-immiscible dye developer, said polymeric layer comprising a coacervate containing a low isoelectric point gelatin and a gelatin derivative which comprises the reaction product of gelatin and a gelatin derivatizing agent which reacts with at least a portion of the amino groups of gelatin to provide neutralization of at least a portion of the positive charges provided to the gelatin molecule, in aqueous solution, by said amino groups.

9. A product as defined in claim 8 wherein said gelatin derivatizing agent comprises a dicarboxylic acid anhydride.

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